Chemistries for Protection and Decontamination

Organic and Inorganic

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William Bell

Report Documentation Page

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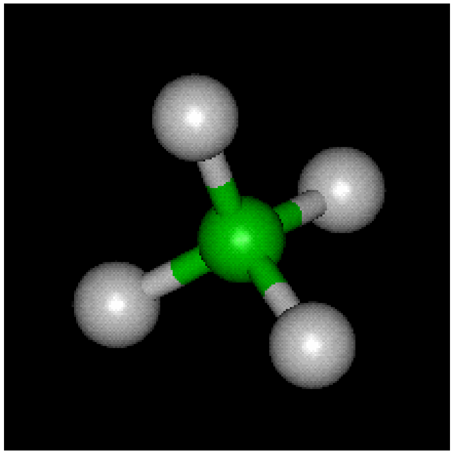
Outline of Presentation

- **Protection**
  - Conductive polymer CW agent sensors for protective clothing
- **Hazard mitigation**
  - Electrochemically generated decon solution
  - Decon assurance spray
  - Catalytic self-decontaminating coatings



Conductive Polymer Sensors

- **Develop nerve agent sensors on an RFID platform for protective clothing**
  - Replace or augment heavy / bulky CWA sensing equipment with active RFID sensors

Integrated with uniform

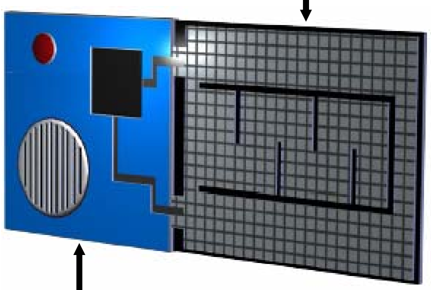
With RFID sensors

Replace (or augment)
Gas chromatographs

Technical Approach

Sensor concept:

(1) an easily printed conducting polymer thin film
(2) that has a selective resistance response to the CWA



Existing RFID technology used to monitor resistance, record data, communicate

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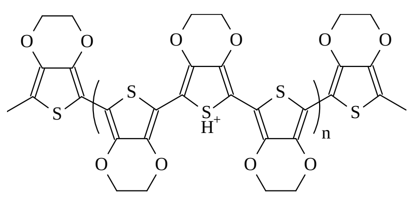
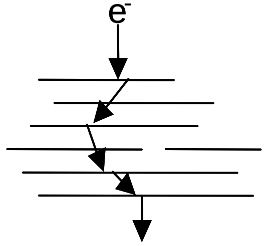
Conducting Polymers: Solubility Problem

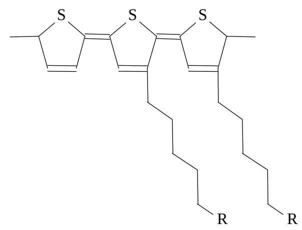
PEDOT
conducting polymer

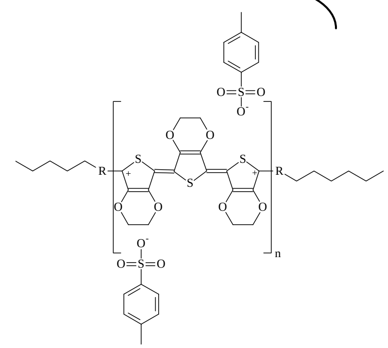


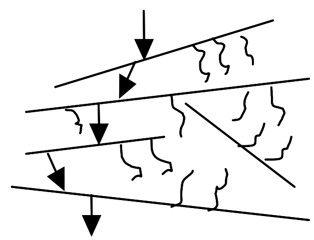


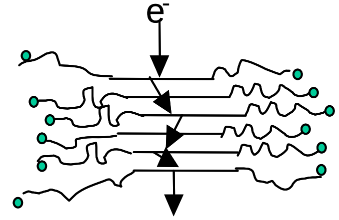
Rigid Rods
crystallize
Insoluble
non-dispersible
intractable

Dispersible forms of polythiophenes









Pendant groups or side groups
promote dispersion in some solvents

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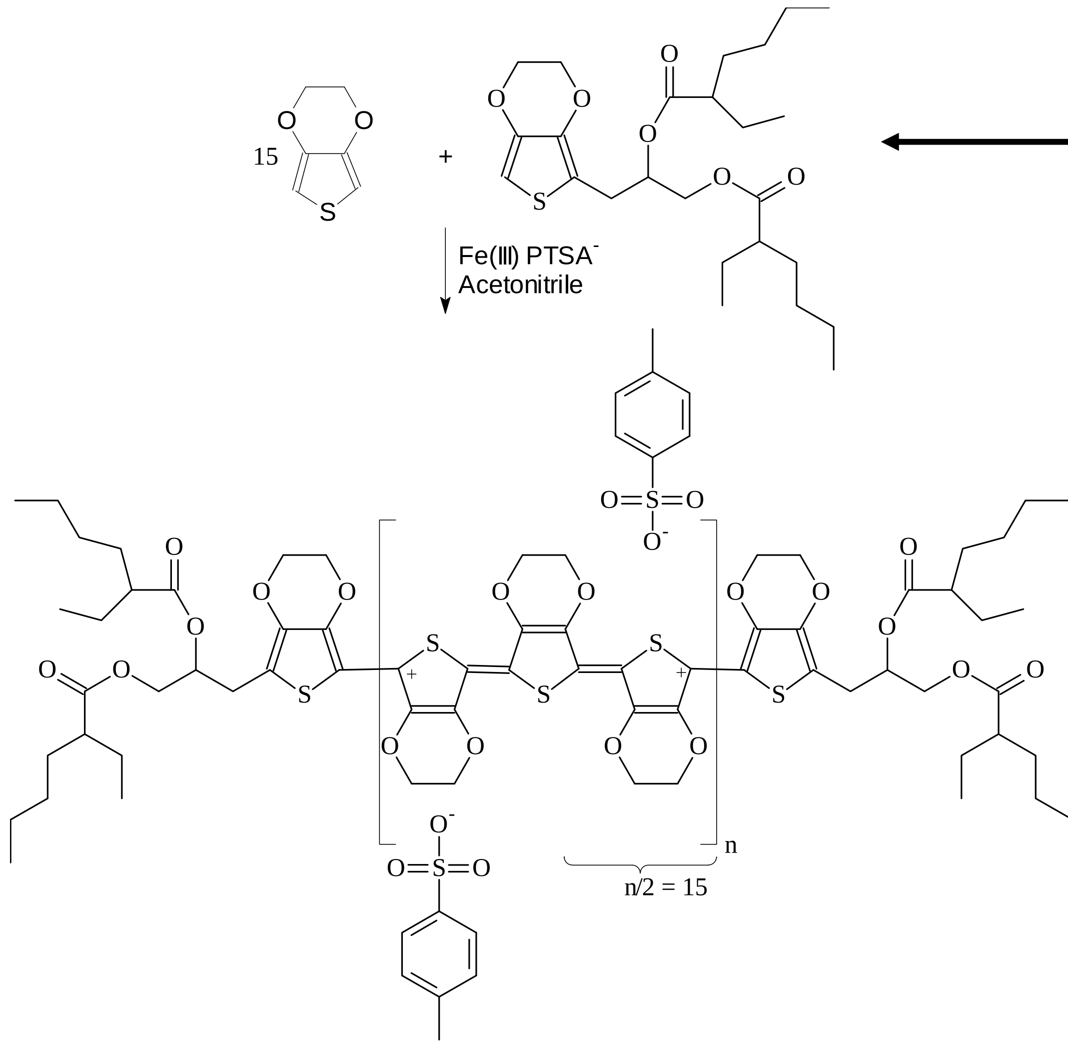
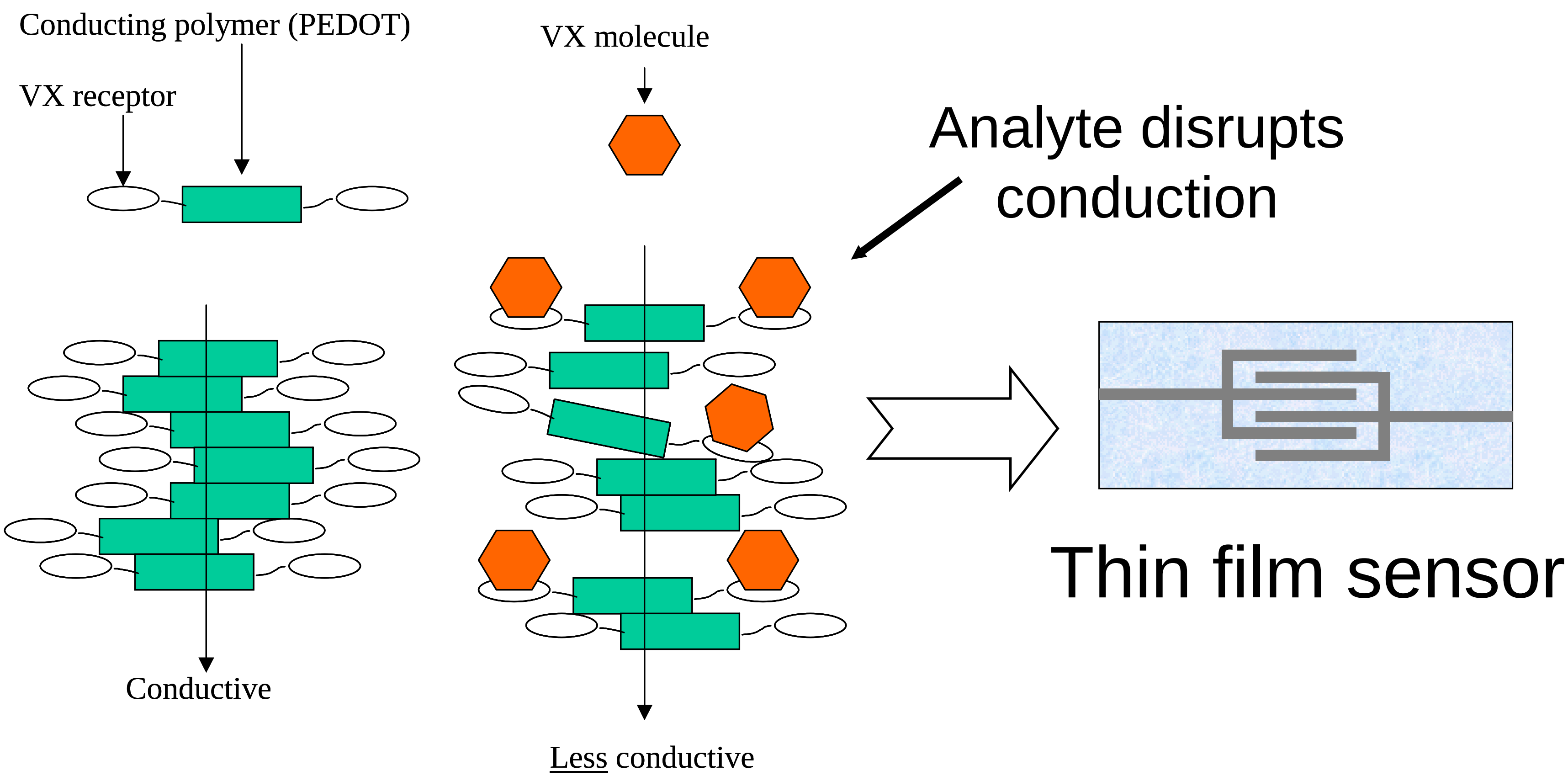
Conducting Oligomers: Co-polymerization of Monomers with End-caps



End capping monomer

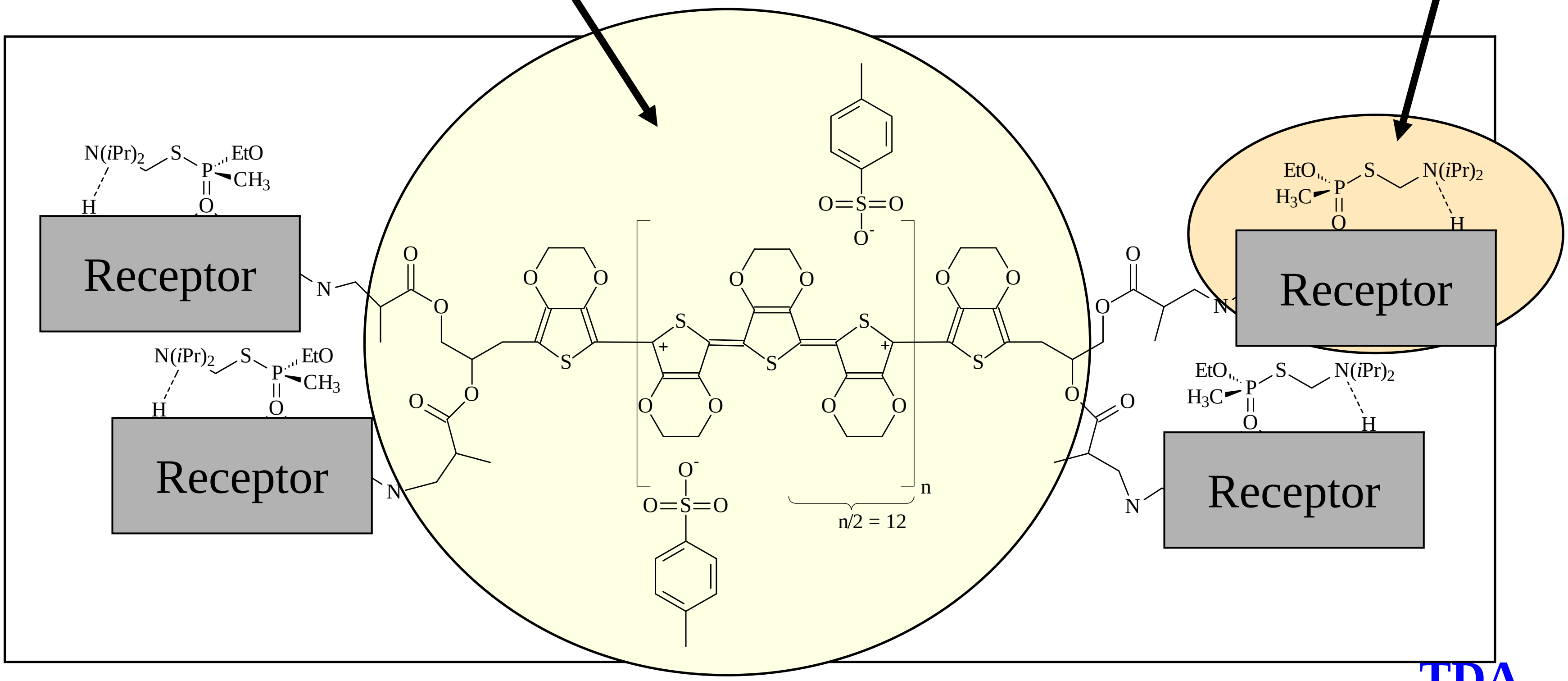
Sensor Concept



Synthetic Approach – Modify a Commercial Product with Receptors

Central core is based on existing TDA conducting polymer materials

Many different receptors can be added and tested



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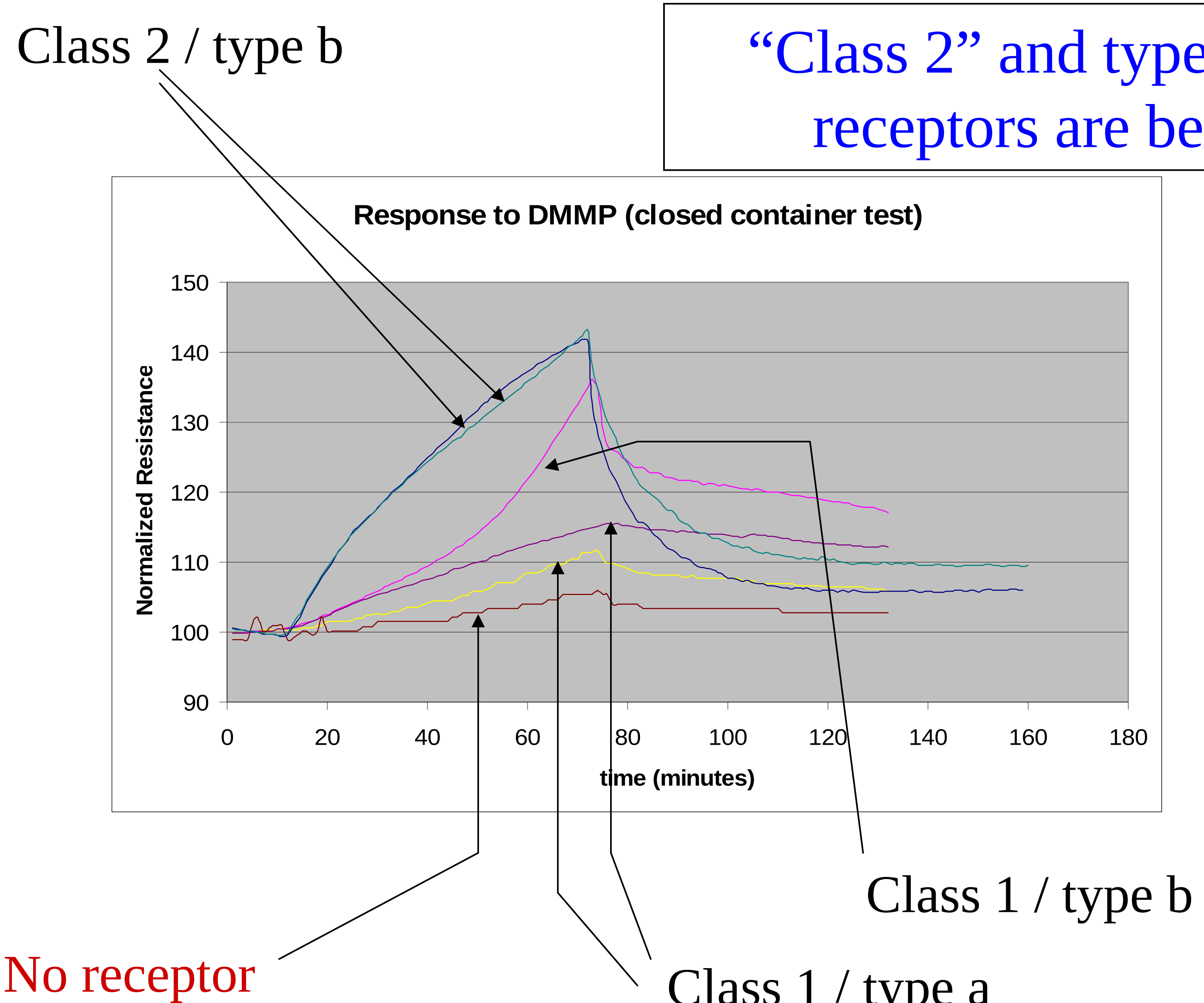
Conducting Polymer Sensors

- **New receptors are conjugated to conducting polymer**
  - Good selectivity
  - Strong function of receptor type
  - Varying the binding strength gives significant DMMP selectivity.
- **Live agent GB test soon for new receptors**
  - Sequential exposure / recovery at two concentrations
    - 500 mg/m3 and 2500 mg/m3
- **Humidity effects have been quantified**
- **New RFID tags will be designed and acquired**
  - Measure and compare two sensor films
  - One with a receptor and one with no receptor (control)
  - Control film will eliminate temperature and humidity effects

Selectivity of Receptors

"Class 2" and type "b" receptors are best



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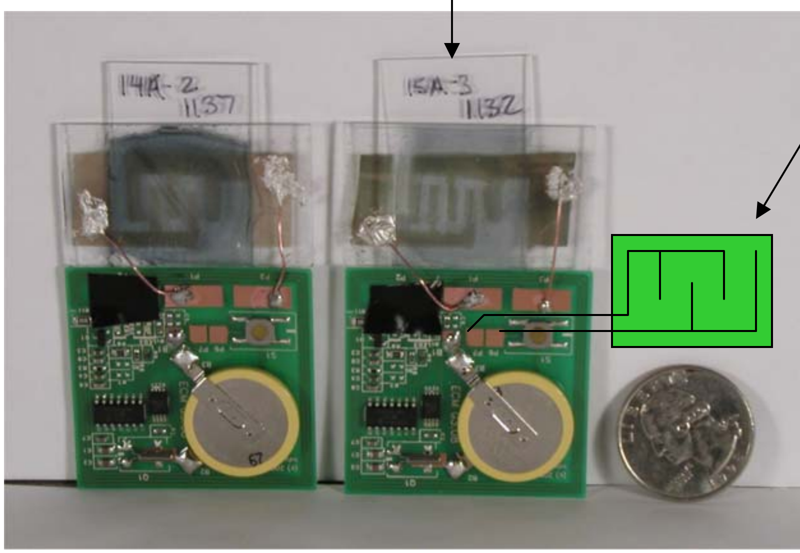
Sensor Corrected for Temperature and Humidity

Current tags measure one film (with receptor)



New tags will add a second film (with no receptor)

Both films will respond nearly the same to temperature and humidity, but the film with the receptor will have a much stronger response to the CW agent.

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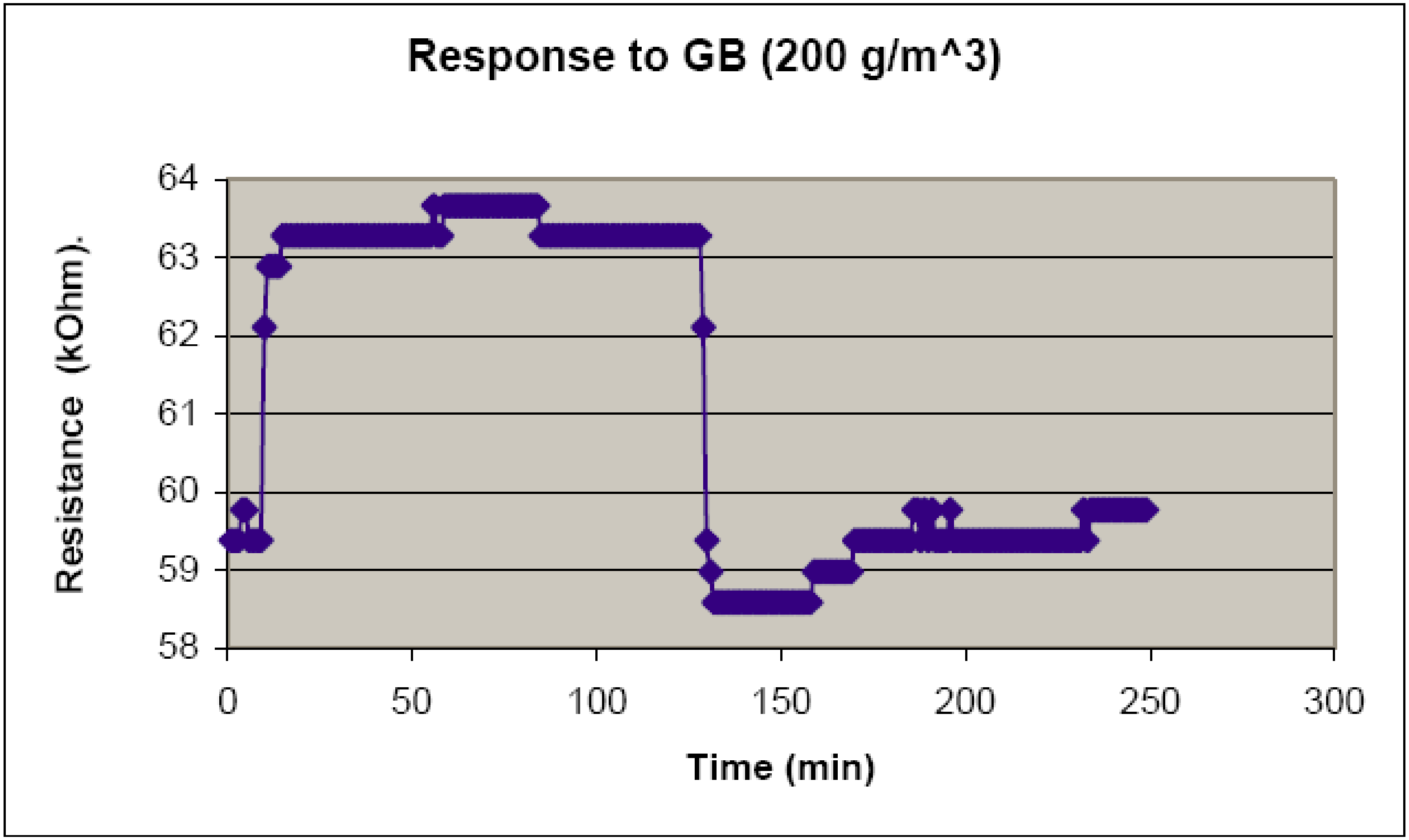
Sensor Response to Live Agent



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Electrochemically Generated Liquid Decon Solution

- **Technology objective: water-based system for operational decon**
  - Rapidly neutralize against CW and BW agents
  - Stable to long-term storage
  - Readily transported
  - Quickly activated
  - Minimal environmental impact
- **Operational decon objectives:**
  - Neutralize classical CW agents in five minutes to below limit of detection with M8/M9 paper
  - Neutralize biological threats, including bacterial spores

Operational Decon

Minimize Contact and Transfer Hazards to Sustain Operations

Approach

- **Generate active species as needed using battery-powered electrochemical cell**
- **Store and transport a powder solid, not a highly reactive species**
  - Shelf stable and readily transportable
  - Add water on site
- **Active species are generated on demand**
  - Highly reactive and do not persist
  - No hazardous residue, environmentally friendly
- **Liquid decon, simple spray on application**

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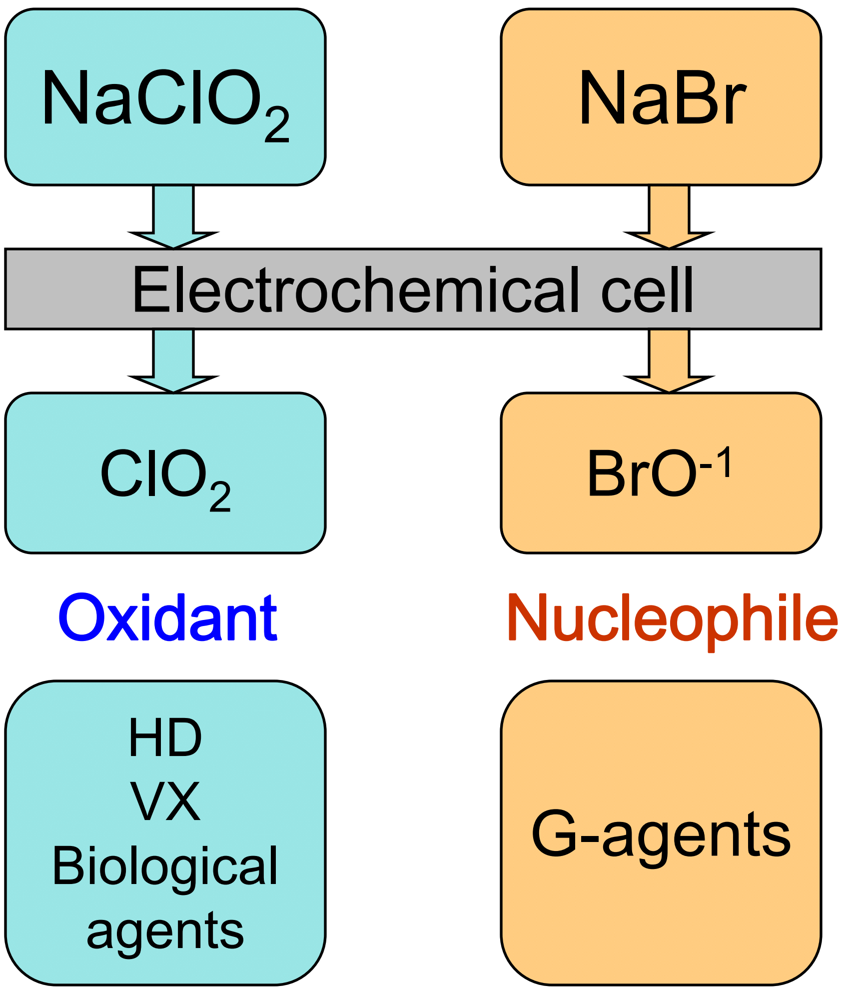
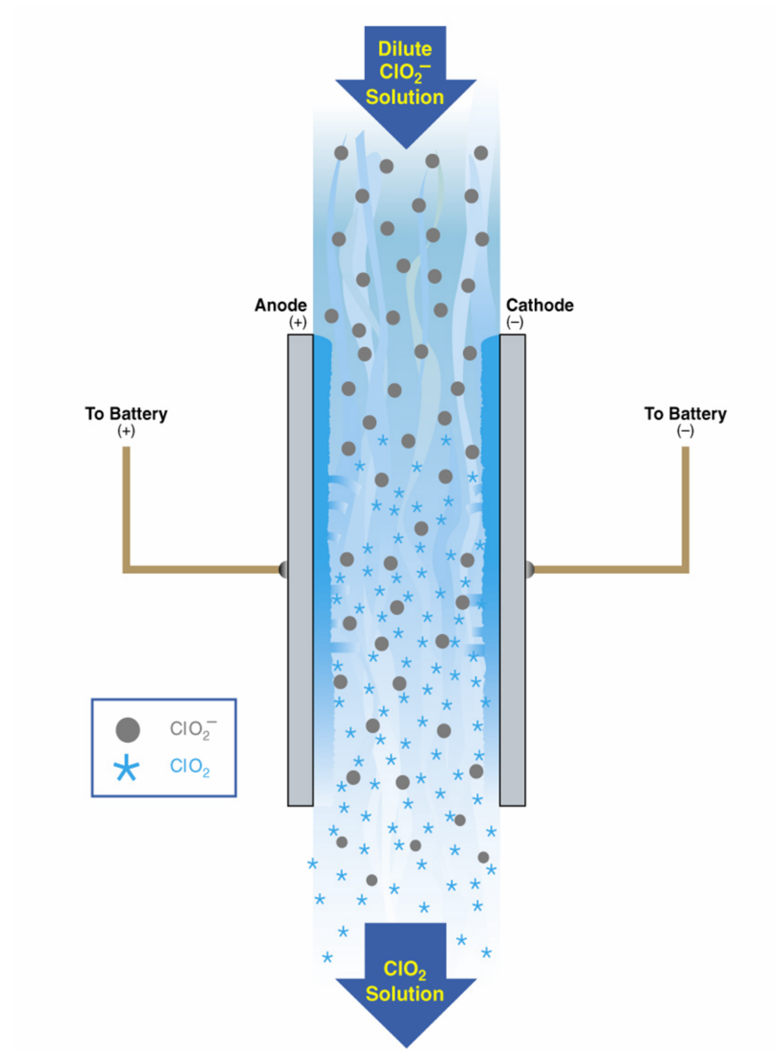
Technology Summary





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Why ClO_2?

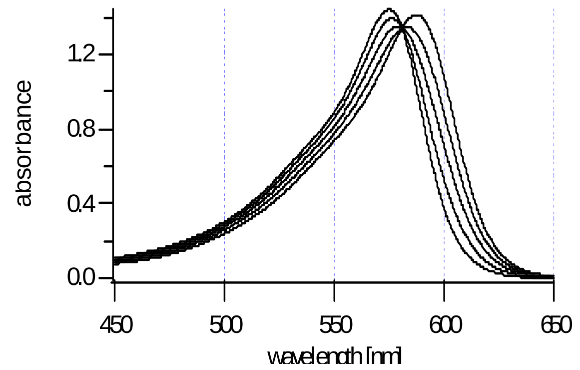
- Neutralizes HD & VX
- Gas is soluble in water and organics
- Decomposes completely in a short time, minimizing environmental hazard
- Chemically effective over a broad pH range
- Known sporicide, bactericide, and viricide

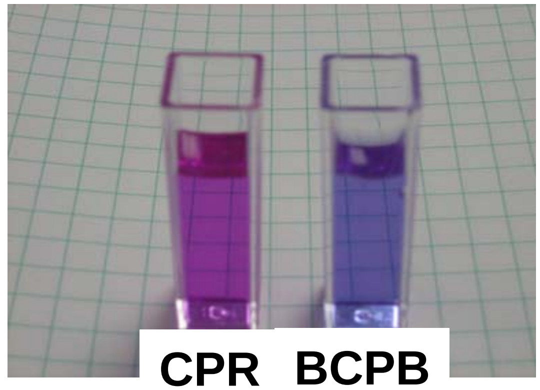
Why BrO^-?

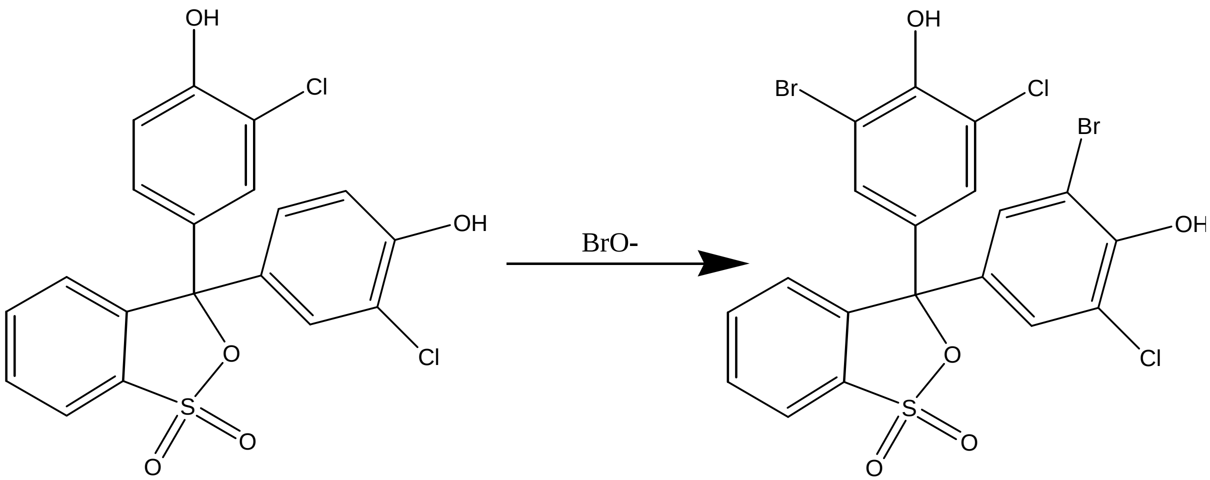
- Rapid GD hydrolysis
- Alpha-effect nucleophile

Analytical Method Development

- **TDA developed methods to quantify BrO^- in presence of ClO_2**
  - Cannot use oxidative property of species to detect BrO^-, ClO_2 is a stronger oxidant
  - Spectrophotometric method uses chlorophenol red (CPR): oxidized in presence of ClO_2, brominated by BrO^-







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Project Status (1)

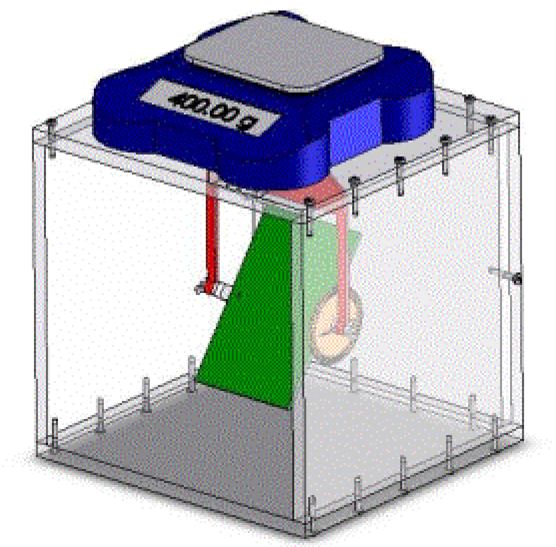
- **Formulation defined**
  - $NaClO_2$, NaBr, plus additives
- **CW agent efficacy for operational decon confirmed through tests with live agents on multiple surfaces**
  - Limited data on efficacy to thorough decon levels
- **Efficacy against biological threats confirmed**
  - Active against bacteria (vegetative cells and spores), viruses. Tests to verify activity against anthrax spores are planned; required for EPA approval as sporicide under FIFRA

Project Status (2)

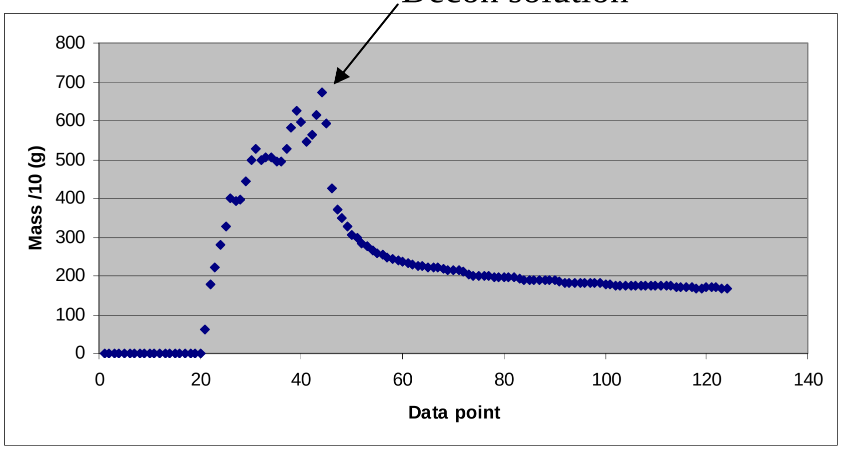
- **Prepared and evaluated test units**
  - Handheld, backpack; larger units feasible
- **Extensive tests of materials compatibility**
- **Optimized spray application; tests underway to compare spray vs. brush**
- **Tests and analysis confirmed that system is stable on storage, readily transported per DOT regulations**
- **System is versatile**
  - Can be used with other solutions, range of sizes

Surface Coverage

- **Tests determined the amount of solution on a CARC-painted surface at different orientations**
  - Determine film volume, thickness. Compare with test data showing efficacy against live agents on same surface, orientation.
- **Determine the volume of solution required for operational decon of a given surface area**
  - Analysis confirmed that a backpack-size unit has capacity to treat one vehicle



Max mass/volume of
Decon solution



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Backpack EC Decon Test Unit

Backpack includes battery, pump, flow controller, electrochemical cell, spray wand. Field test with full strength solution.

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Decontamination Assurance Spray

- Post decon treatment to identify problem areas
- Designed to be compatible with available sprayers
- Apply to all types of surface
- Current systems, such as M8/M9 papers and test kit, must be applied to a specific spot; this system could cover an entire vehicle or piece of equipment

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Design Parameters

- Color change in contaminated areas
- Visible on all surfaces
- Non-Staining
- Responsive to CW agents
- Responsive to many TICS?
- Answer: develop a white powder-supported colorimetric indicator

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Approach to Development of Colorimetric Indicator

- **Formulate from commodity chemicals**
  - Lower cost, faster time to product
- **Design a complex that releases a dye after reacting with CW agents (and TICs)**
- **Study reactivity with simulants**
- **Multiple colors possible**
  - Possible selective color responses to identify different agents
- **Measure reaction rates**
  - Both absorbance and reflectance
- **Formulate as spray**

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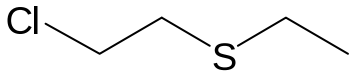
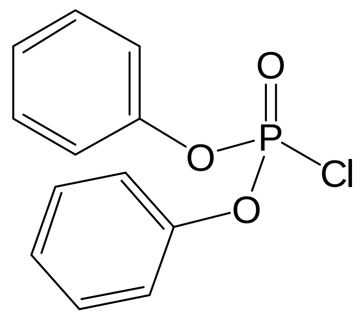
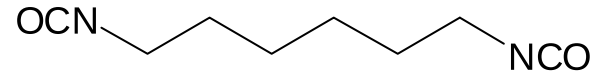
Simulants



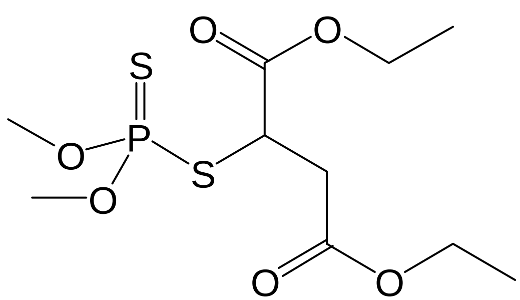
CEES



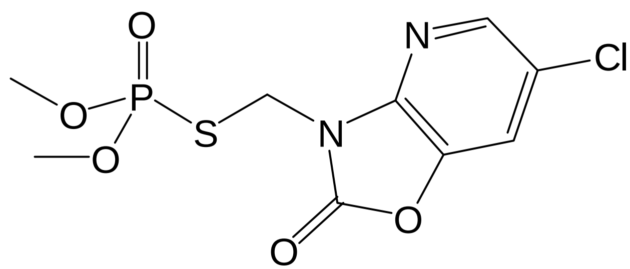
Diphenyl Chlorophosphate



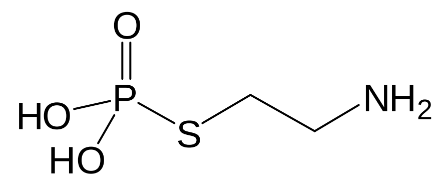
HMDI



Malathion



Azamethiphos



Cysteamine S-Phosphate

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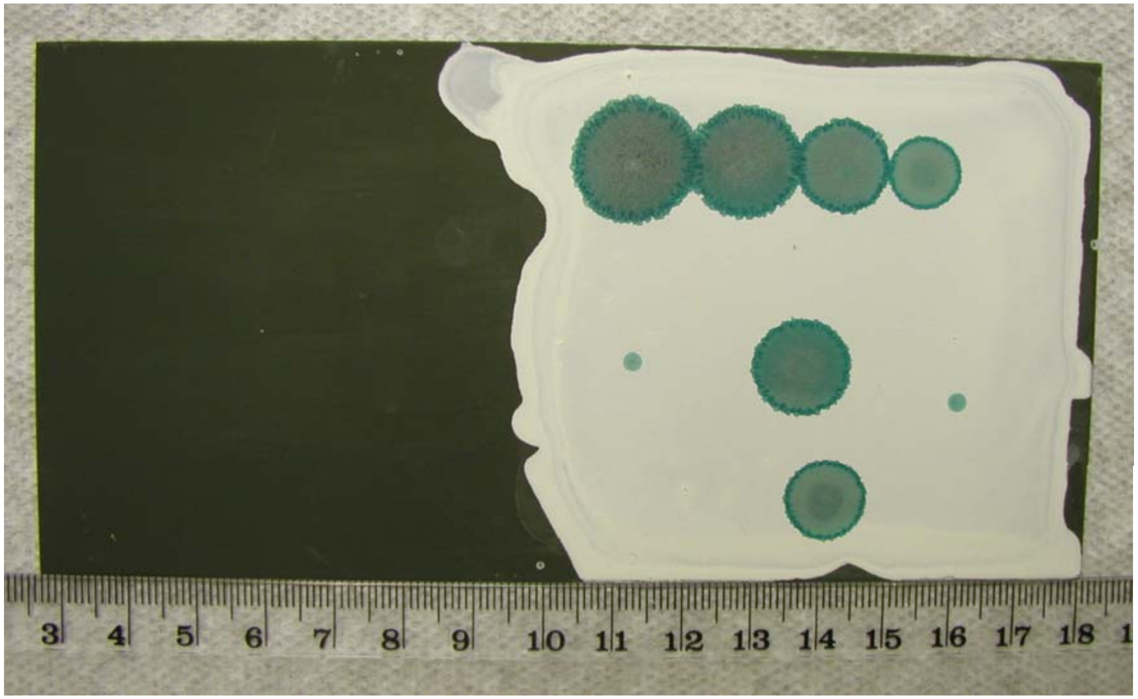
Support Indicators on a White Powder

- **A white powder provides color contrast so that color changes are visible on all surfaces**
  - The powder retains all of the colored material to avoid staining
  - Agent is absorbed into the powder support, increasing the interaction with the indicator



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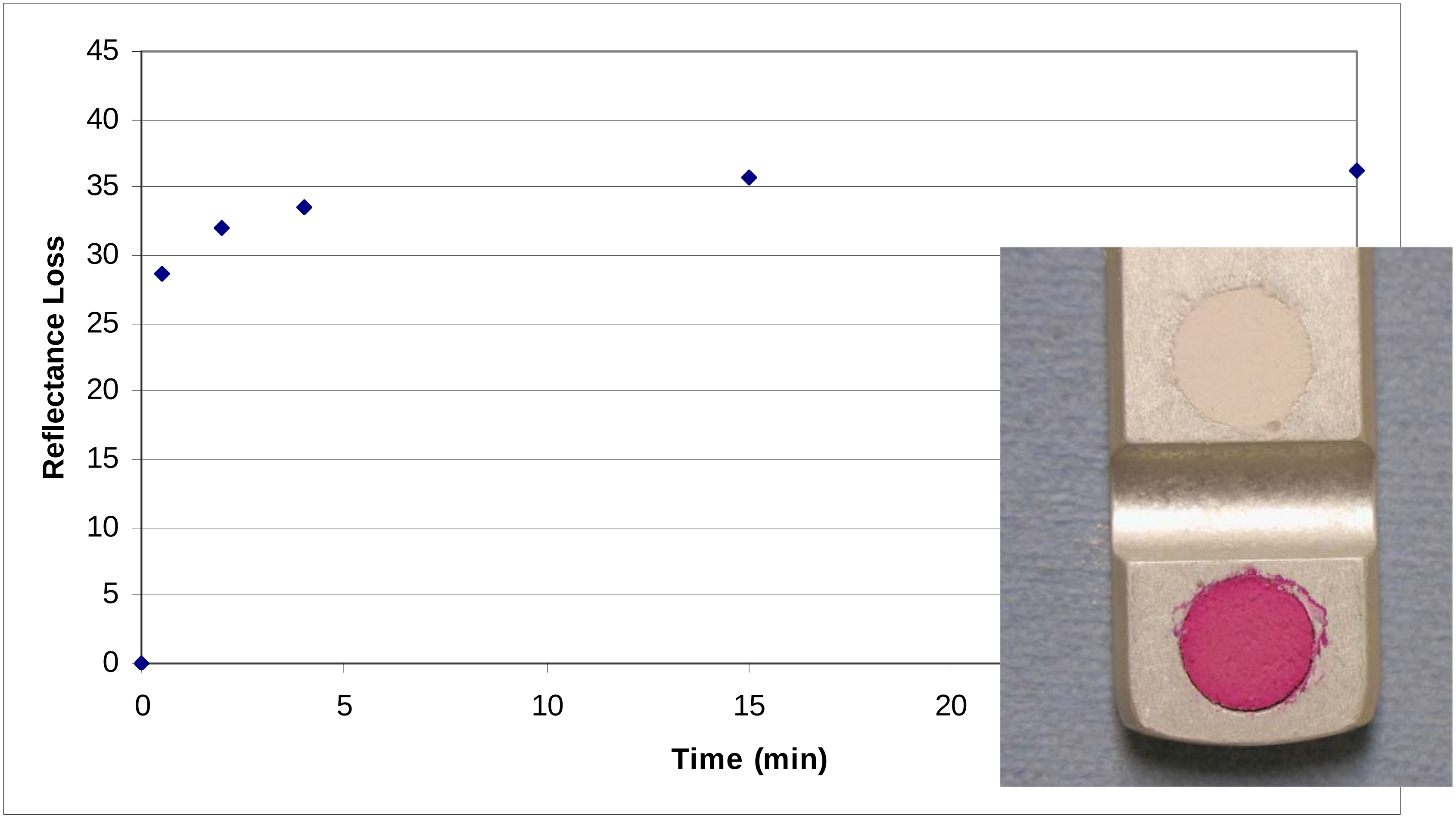
Red Indicator with 4% Azamethiphos in Ethanol



Further Directions

- Improved loading of the indicator on supports
- Improved reactivity of supported indicator
- Live agent validation
- Development of a sprayable formulation

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Catalytic Self-Decontaminating Coatings

- **Goal: coating that will self-decontaminate through catalytic reaction at ambient temperature**
- **Effective against VX, G-agents, and HD**
  - Activity against BW agents not considered here
- **Objective is non-hazardous products, not complete mineralization**
  - TDA's effort does not consider photochemical processes
- **Focus on selective oxidation of HD to sulfoxide**

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Application: Military Ground Vehicles

Aircraft, Other Sensitive and High-value Assets

- **Currently use chemical agent resistant coating (CARC)**
  - Absorbs minimal amount of CW agents
  - Epoxy primer for corrosion protection
  - Polyurethane topcoat; light-stable, camouflage (visible and NIR)
  - Any modifications must maintain current features of CARC coating system

HMMWV could benefit from catalytic coating

TDA Research

Structured Surface

An Approach to Increasing Effective Catalyst Surface Area

- **Advantage of a catalytic coating with a porous surface is improved mole ratio of HD to catalyst compared to non-structured surface**
  - Heavy coverage: 400
  - Light coverage: 100
- **Increase the number of accessible catalyst sites per nominal surface area by a factor of 80 or more**
  - Corresponding decrease in turnover number required for complete decontamination
- **Structured catalyst consistent with signature management**
  - CARC uses particulate materials (flatting agents) to lower gloss
- **Simplify experimental challenge of evaluation**
  - Lower turnover rates are measurable

Test Methods

- **Test with simulants, then live agents**
  - Identify reaction products
- **Test sequence:**
  - Stirred homogeneous solution
  - Stirred dispersion (substrate soluble, not catalyst)
  - Solvent-free (stirred dry powder)
  - Coated metal panels
- **Challenge: follow reaction progress in sealed vessel**
  - Monitor changes in volume or pressure
  - In oxidation reactions, O_2 is converted to a non-volatile product, so the pO_2 and total pressure will change
- **At 5:1 mole ratio O_2:CEES, 13% of CEES is in vapor phase**
  - At this loading, 4% of the air will be consumed at the end of the reaction

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Oxygen Uptake Apparatus

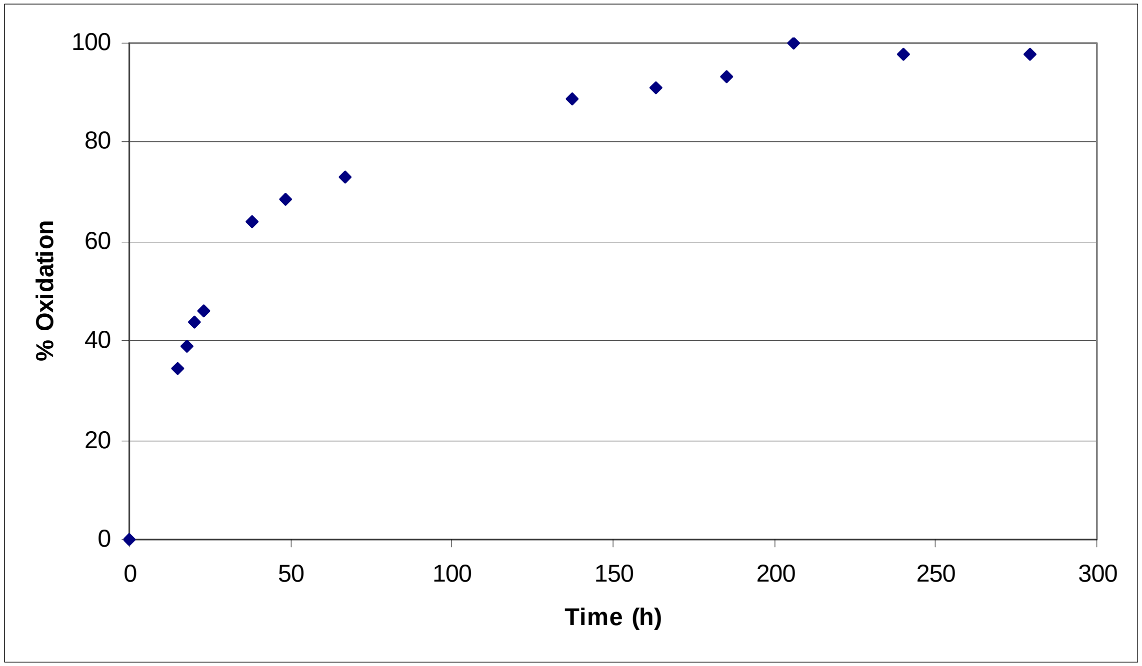
- Dual gas burettes partially filled with oil
- One flask holds the stirred catalyst/substrate and the other is a reference flask
- Both flasks sealed at same time with identical initial volume, temperature and pressure
- Uptake measured by change in volume at constant pressure

Measurement of Catalyst Activity, Supported Catalyst in Solvent

- **Stirred heterogeneous mixture**
- **CEES as simulant**
- **Monitored reaction by GC analysis of aliquots**
- **Observed 55% removal in 2 hours, 100% removal (~23 catalyst turnovers) in 3 days.**
- **CEES sulfoxide detected after reaction**

Measurement of Oxygen Uptake, Supported Catalyst and CEES in Solvent-Free System

- Supported catalyst as powder, neat CEES; mechanical agitation
- Catalytic oxidation of CEES; ~20 turnovers
- Oxidation stops after conversion of sulfide to sulfoxide



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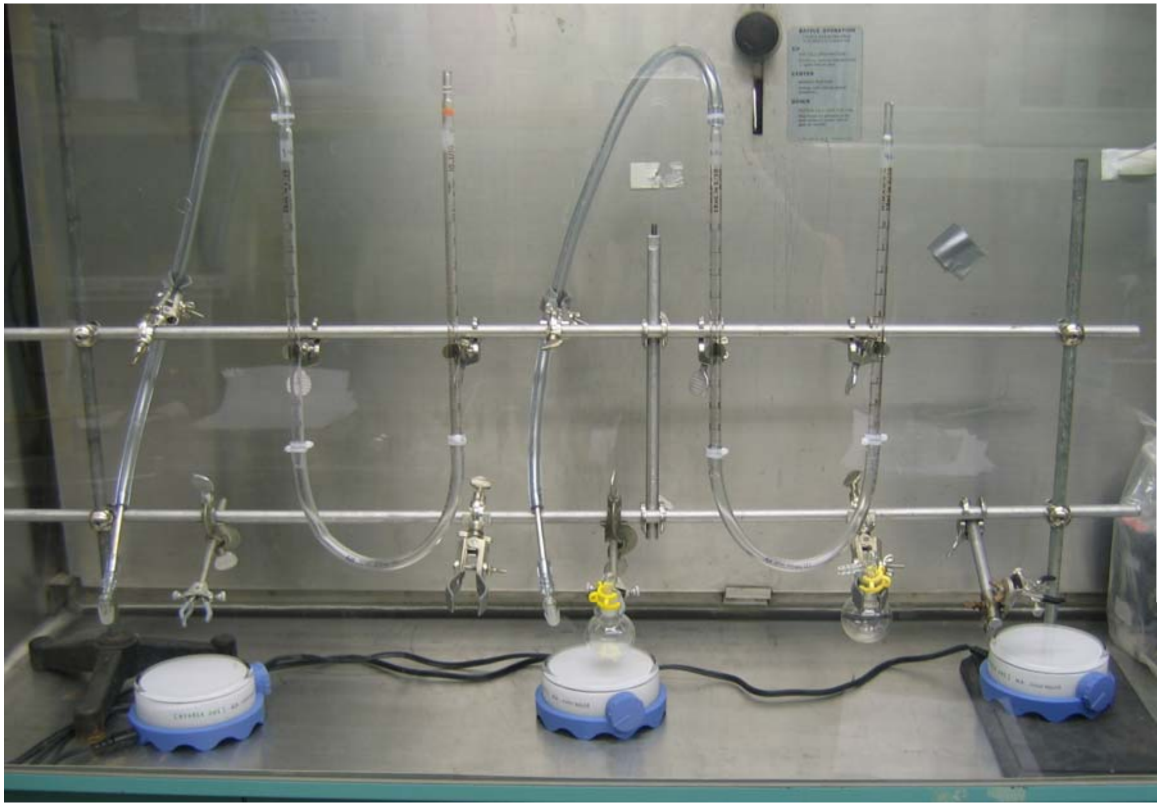
Tests with HD

- At CUBRC (Buffalo)
- Supported catalyst as powder, neat HD; mechanical agitation.
- Ambient temperature, sealed vessel under air, 28-hour test
- Only partial recovery (~40%) of HD in control (support only); much lower recovery in presence of supported catalyst (~5%)

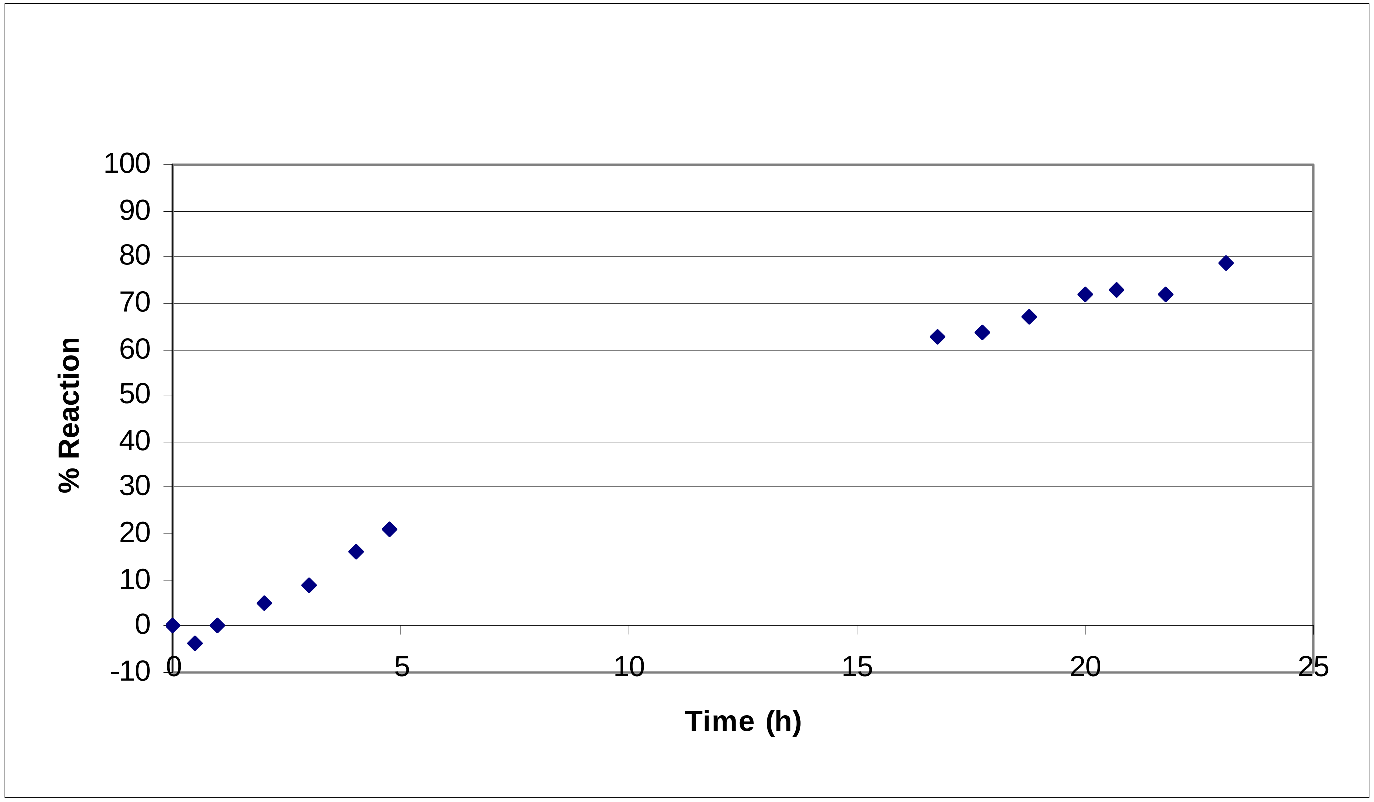
Tests with HD



Assembly of two dual gas burettes for HD tests at CUBRC. The dual burette on the left was connected to a flask with the catalyst and HD (and to an empty flask as a pressure reference). The dual burette was connected to a flask that held untreated catalyst support and HD.

Measurement of Oxygen Uptake, Supported Catalyst and HD in Solvent-Free System

- Supported catalyst as powder, neat HD; mechanical agitation
- Based on difference between HD recovery with catalyst and control, 6 to 7 turnovers
- After extraction, HD-sulfoxide found in supported catalyst sample, not in control
- Faster rate than earlier test with CEES; modified catalyst



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Catalytic Coatings: Summary

- **Structured surfaces could improve catalyst loading and performance in reactive coatings**
- **Use of O_2 uptake measurement to follow course of oxidation reactions**
  - TDA tested catalysts in fluorocarbon slurry and dry powder, with CEES and HD
  - Test with HD showed oxygen uptake and sulfoxide formation consistent with aerobic oxidation
- **Preparation of catalyst samples on epoxy-coated metal coupons**
  - Demonstrated activity with CEES

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  - CUBRC: Meg Stapleton, Rich Fitzpatrick
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  - ARO: Jennifer Becker, Stephen Lee
  - DTRA: Charles Bass, Mark Mueller, John Weimaster
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